

# Catalytic Reduction of NOx

Dhruv Gupta, Smarthveer Sidana, Vani Batra, Aneerendra

**Abstract**— Improving efficiency of catalytic reduction of NOx at post- combustion stage

**Index Terms**— Ammonia Slippage, Catalytic Reduction, Combustion, Reduction

## 1 INTRODUCTION

Nitrogen Oxides (NOx) and Sulphur Dioxide (SO2) are emitted from boilers, coal based power plants, diesel locomotive and engines (like those on ships), automobiles, gas turbines etc. NOx are one of the reasons for the formation of acid rain, photochemical smog and ground level ozone.

Treatment of these oxides is getting extensive attention over last few decades due to growing environmental concern and awareness. Limits to these emissions has been set and revised continuously by the government. More and more research is going on to get cost effective methods of achieving this.

Three sites where we can check NOx are pre-combustion (decrease the amount of Nitrogen in fuel), during-combustion (change the engine condition so that less NOx is formed) and post-combustion (treat thee exhaust gas from the engine). Both pre-combustion and during combustion techniques, when applied practically, give about 50% reduction in NOx emissions whereas treatment of exhaust gas gives efficiency up to 90%. So we focus on post-combustion perfection.

## 1 TERMINOLOGY

### Selective Catalytic Reduction(SCR)

It is a process of converting NOx, with help of certain catalyst, to Nitrogen and water, using gaseous reductants like ammonia (may be obtained from urea) which are injected into the inlet stream of SCR equipment. It reduces NOx "selectively".

### Reactions over NSR catalyst.

Engine cycle	Reaction over Pt	Role of BaO
Lean cycle	$NO + O_2 \rightarrow NO_2$	Stored NO <sub>2</sub> as nitrates
Rich cycle	$HC + NO_2 \rightarrow N_2 + CO_2 + H_2O$	Released nitrates as NO <sub>2</sub>
	$H_2 + NO_2 \rightarrow N_2 + H_2O$	
	$CO + NO_2 \rightarrow N_2 + CO_2$	

### Ammonia slippage

The amount of ammonia leaving from the NH3-SCR equipment unreacted. This acts as a feedback and we can design closed loop system for controlling the amount of ammonia injected. Closed loop systems maximises efficiency, thus lowering costs.

### NOx Storage Reduction (NSR)

Lean NOx Traps (LNT). Using different cycles of engine in this method NOx is stored on BaO in one cycle and then reduced in the other from partial combustion fumes. It is very similar to HC-SCR.

## 3 INDUSTRIAL PROCESS/CHEMICAL SYNTHESIS AND ITS USES

As mentioned above any plant with boilers or those which use coal/gasoline burning to drive some system need a module to treat their emissions to meet the norms. Ammonia based SCR is very popular in this case as the temperature requirement for that is optimum with temperatures from boilers. As a product we get N2 and H2O.

**We will be focusing mainly on SCR.**

## 4 REDUCTANTS

1. Anhydrous Ammonia: This is extremely dangerous to store and transport but can be used readily in the reaction.
2. Aqueous Ammonia: Relatively safe to store and

transport but has to be evaporated to be used in the reactor.

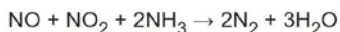
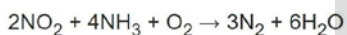
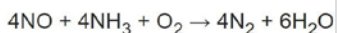
- 3 Urea: Easiest to store and transport but has to be thermally decomposed to be converted to ammonia. Also CO<sub>2</sub> is released during decomposition. DEF (Diesel Exhaust Fluid) is an aqueous solution of 32.5% urea and 67.5% deionized water. It is used to operate SCR converters in motor vehicles with diesel engines.
- 4 Hydrocarbons
- 5 Hydrogen: Relatively new technology and costly in case of operation as it requires noble metals (Pt,Pd) to work as catalysts.

## 5 INLET STREAM

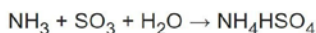
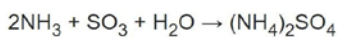
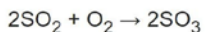
SCR module requires a particulate free inlet stream because they block reaction sites on the catalysts and may even react because of oxidizing environment. Fouling with PM is the main reason for short life of catalysts.

## 6 REACTION SEQUENCE

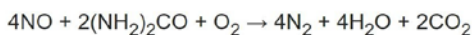
The overall reaction is as follows



With several secondary reactions:



The reaction for urea instead of either anhydrous or aqueous ammonia is:



## 7 CATALYSTS USED

There is basically three class of catalysts that could be used v.i.z. Metals, Metal oxides and Zeolites. What we deploy totally depends upon the requirements, working conditions, cost of our system and other factors. So mechanisms also vary with different combinations of

reducing agent and catalyst we use. Some catalysts are listed

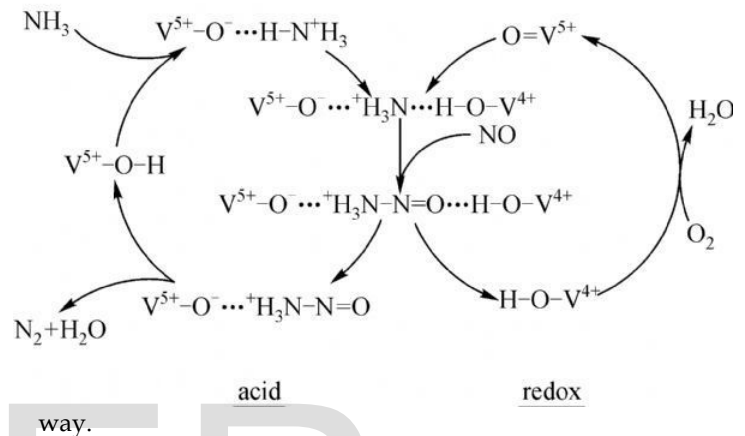
**Metals:** Ag/MgO-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Pt, Ti, In.

**Metal Oxides:** V<sub>2</sub>O<sub>5</sub> mixed with WO<sub>3</sub> and/or MoO<sub>3</sub> (as promoters) supported on TiO<sub>2</sub>.

**Ion exchanged Zeolites:** Fe-ZSM 5, Cu-ZSM 5.

Often we see an optimum mix of two or more catalyst or class of catalysts employed to do the job in best possible

### DeNO<sub>x</sub> catalytic cycle



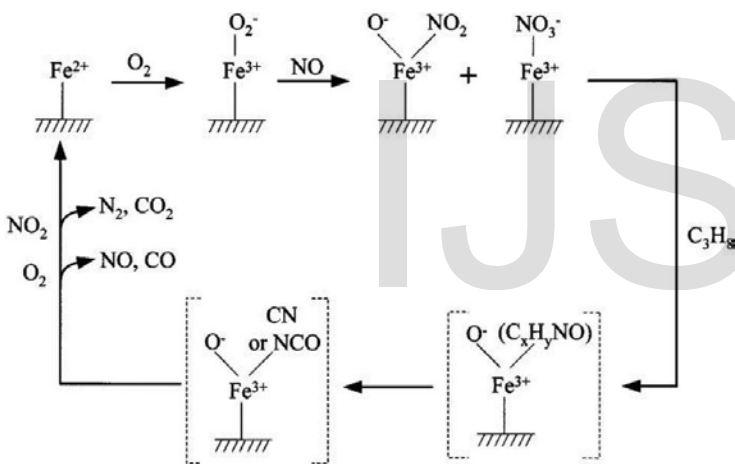
## 8 MECHANISM AND ROLE OF THE CATALYST

1. First we will look into the mechanism using V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> as a catalyst supported on TiO<sub>2</sub>. We can see that in the acid cycle Ammonia is chemisorbed on the oxide. Also experimental data tells that V<sub>2</sub>O<sub>5</sub> supports adsorption of NO to a very little extent. So this heterogeneous catalysis mainly follows Eley-Rideal mechanism in which one of the reacting species in gas phase collides with the other in adsorbed phase. So the rate of the reaction depends mostly on the concentration of gas phase species (NO) linearly and a little on the adsorbed phase (NH<sub>3</sub>) asymptotically. So the order of the reaction w.r.t NO comes out to be 1 (checked experimentally). We observe from the mechanism that the catalyst helps in breaking of the bond between N and O in NO. The bond order first reduces by one, then we have positively charged Nitrogen pulling the electrons in the NO bond.

2. Next up we will look on the reduction of NOx using hydrogen as a reductant. The process is also known as H2-SCR. As described earlier these work best with noble metal catalyst, Pt has been used here for explanation. Here the fact used for reduction is that absorbed Hydrogen is one of the best reducing agents.

Both NO and H2 adsorb on Pt surface and then multiple reaction may occur. So in this case we have Langmuir-Hinshelwood mechanism in which both the reacting species react in the adsorbed phase. One can clearly figure it out that adsorption helps in cleavage of the NO bond which is crucial to NOx Reduction.

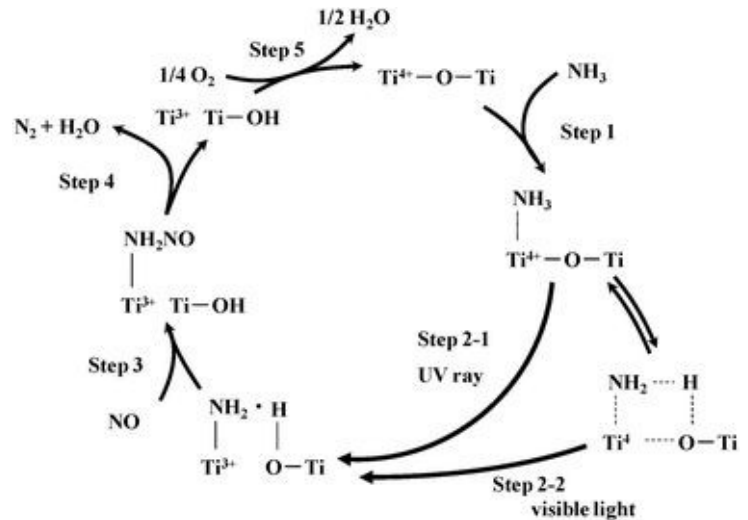
3. Now we will discuss HC-SCR in which hydrocarbons are used as a reductant. This method could play a vital role in engine design with inbuilt reducers as one can use the unburnt hydrocarbons



from fuel (very similar to NSR).

Catalyst used here is an iron exchanged zeolite (like Fe-ZSM5). The basic mechanism is quite similar to that of vanadia type catalysts but here we have NO adsorbing and hydrocarbon attacking from the gas phase. It decreases the bond order of NO bond and lead to formation of cyanide or isocyanide which decomposes to give N2. Major drawback of the process being used as a post combustion method is less selectivity of Hydrocarbons to N2. Only one-tenth of HC is used for reduction and rest is burnt to form CO2.

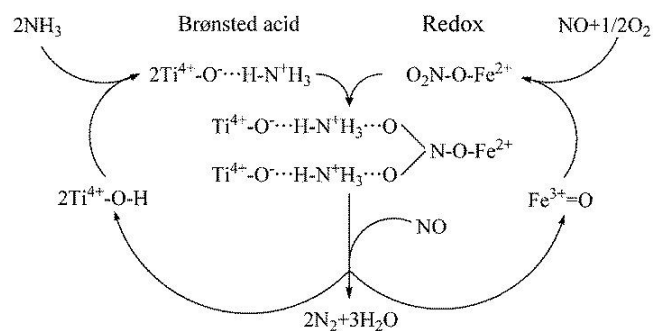
4. Lastly, we will look into NH3-SCR using TiO2 as a catalyst. The ER mechanism is quite similar to that of vanadium catalyst. In both cases we have a redox site and acidic site. In the LH mechanism we have both NO and NH3 adsorbing on the surface.



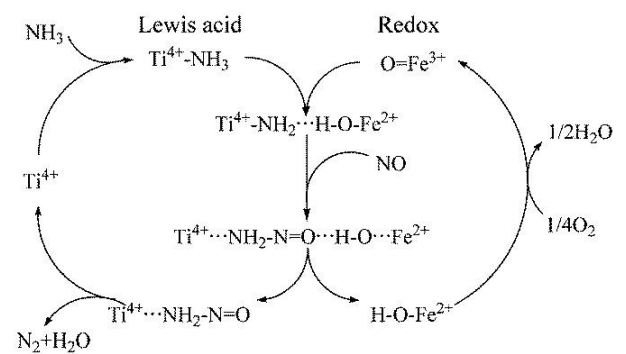
Oxidation of NO is also observed here. Other difference between the two is the nature of the acidic sites (one being bronsted, the other lewis).

One of the general features of these catalytic reduction is that they follow LH mechanism at low temperature and ER mechanism at high temperature. So as the temperature is increased the order of the reaction w.r.t. NO becomes closer to 1. The following graph shows the results with CN 500 catalyst

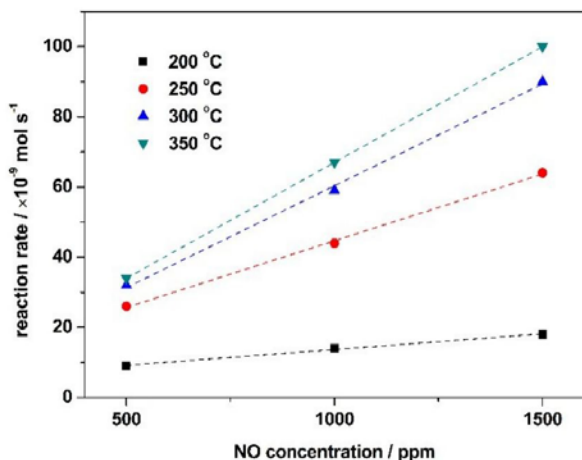
### (A) L-H mechanism at low temperature



### (B) E-R mechanism at high temperature



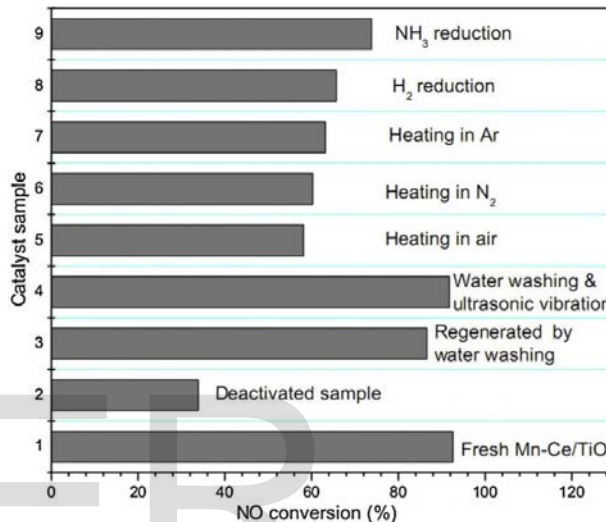
is the reaction scheme of fast SCR over Fe-Zeolite.



Different catalysts show different graph for this type of analysis i.e. some follow ER mechanism even at low temperatures. So the choice of catalyst will also depend upon the rates one wants for their system. One other process worth mentioning is “fast” SCR. The above reaction mechanism is given for vanadium based catalyst It can be clearly observed that the presence of NO allows the conversion of ammonium nitrate formed in the first step. It has been experimentally observed that the rates of reaction are maximum in case of equimolar concentration of NO and NO<sub>2</sub> rather than using only NO or NO<sub>2</sub>. Fast SCR play an important role during temperatures between 443 K to 463 K were ammonium nitrate formed from disproportionation etc. reacts with NO to convert to N<sub>2</sub> and H<sub>2</sub>O. The Following

### 9 CATALYSTS USED

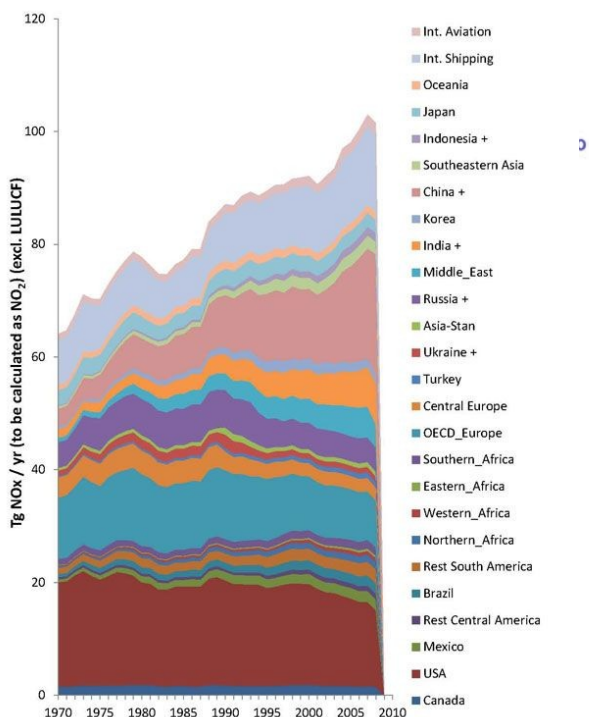
One of the major reasons for catalysts in NO<sub>x</sub> reduction going out of service is SO<sub>2</sub> poisoning. For Fe or Cu Zeolites there is formation of sulphate which are quite stable and thus block the active sites permanently. So there are many methods for regeneration of the catalysts. The following graph shows typical results for Magnese based catalyst.



We also need better low temperature catalytic converters to be employed in automobiles because temperatures during short rides don't go up to that of working conditions of conventional catalysts.

### 10 IMPACT

NO<sub>x</sub> emission during recent years is given the graph. We have been doing harm to environment for too long. In recent times we have seen nature on payback mode. Delhi has been smoked from its worst smog ever. Pollution levels are too high. This calls for active steps towards our redemption. Efficient catalytic converters are the future of the automobile industry. It is expected to by 10% in next five years and a market of 150 million unit till 2019.



## REFERENCES

- [1] Wikipedia:- [https://en.wikipedia.org/wiki/Selective\\_catalytic\\_reduction](https://en.wikipedia.org/wiki/Selective_catalytic_reduction)
- [2] <http://www.tri-mer.com/low-temperature-SCR.html>
- [3] Xingxing Chenga and Xiaotao T., Bi Review A review of recent advances in selective catalytic NOx reduction reactor technologies.
- [4] Ruiyang Qu, Yue Peng, Xiaoxu Sun, Junhua Li, Xiang Gao and Kefa Cen, Identification of the reaction pathway and reactive species of the selective catalytic reduction of NO with NH3 over cerium-niobium oxide catalysts.
- [5] Royal society of Chemistry for most of the mechanism pictures.
- [6] Cristian Ciardelli, Isabella Nova, Enrico Tronconi, Daniel Chatterjee, Thomas Burkhardt and Michel Weibel, NH3 SCR of NOx for diesel exhausts aftertreatment: role of NO2 in catalytic mechanism, unsteady kinetics and monolith converter modelling.
- [7] Antonio Grossale, Isabella Nova and Enrico Tronconi, Role of Nitrate Species in the "NO2-SCR" Mechanism over a Commercial Fe-zeolite Catalyst for SCR Mobile Applications.
- [8] <http://www.marketsandmarkets.com/PressReleases/catalytic-converter-systems.asp>

IJSER